
THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

THE CYANINE DYES AND RELATED COMPOUNDS

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THE CYANINE DYES AND RELATED COMPOUNDS

This is the eighteenth volume in the series

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

A SERIES OF MONOGRAPHS

ARNOLD WEISSBERGER, *Consulting Editor*



The Chemistry of Heterocyclic Compounds

The chemistry of heterocyclic compounds is one of the most complex branches of organic chemistry. It is equally interesting for its theoretical implications, for the diversity of its synthetic procedures, and for the physiological and industrial significance of heterocyclic compounds.

A field of such importance and intrinsic difficulty should be made as readily accessible as possible, and the lack of a modern detailed and comprehensive presentation of heterocyclic chemistry is therefore keenly felt. It is the intention of the present series to fill this gap by expert presentations of the various branches of heterocyclic chemistry. The subdivisions have been designed to cover the field in its entirety by monographs which reflect the importance and the interrelations of the various compounds, and accommodate the specific interests of the authors.

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ARNOLD WEISSBERGER

Preface

The author's introduction to research in the summer of 1917 at Cambridge, under Sir William Pope and Dr. W. H. Mills, began with the preparation of a series of isocyanines, followed by the establishment of the constitution of Pinacyanol. Seven years' research on cyanines in the Cambridge University Chemical Laboratory were followed by a few months in the Davy Faraday Research Laboratory of the Royal Institution. Then came 5½ years with Ilford Ltd., 18½ years with Kodak Ltd., and, through the kindness of Sir Patrick Linstead, six years at the Imperial College. During these 37 years devoted to cyanines, either in research or in their preparation for industrial use, notes on the published methods had accumulated. This book was begun with the feeling that it would be a great waste *not* to put the information on record, as it might be useful to others working on the subject. The author little thought that the writing would take another 5½ years! An attempt has been made to cover the literature up to the end of 1959.

Emphasis has been laid on the preparative methods rather than on the theoretical aspect of the subject. The first chapter is mainly introductory, explaining the connection of the cyanines with photography, summarising their early chemistry and following with an account of the pioneer work on the constitution of typical cyanines. Apocyanines, in which the nuclei are directly linked, are included in this first chapter. Methincyanines, in Chapter II, are grouped according to methods of synthesis, each group being subdivided according to the type of dye, and this is the system followed throughout. Chapter III deals with methincyanines which are substituted on the chain. Chapters IV and V cover, respectively, symmetrical and unsymmetrical trimethincyanines having an unsubstituted chain, whilst chain-substituted trimethincyanines are described in Chapter VI. In Chapter VII, on pentamethincyanines, both symmetrical and unsymmetrical types, including those with substituents on the chain, are considered. The same applies to Chapter VIII on heptamethincyanines; cyanines with still longer chains are included in that chapter. In the cyanines of

Chapter IX, the odd-numbered carbon chain, which links the nuclei, is cyclic, or part of it is. Chapter X deals with the variations in the nuclei which enter into cyanine molecules, including the use of unusual nuclei. Bases, of which cyanines are the quaternary salts, are in Chapter XI. Chapter XII comprises azacyanines where one or more $\text{:CH}\cdot$ groups of the chain are replaced by :N . Numerous types of dyes related to cyanines are gathered together in Chapter XIII and include *p*-dimethylaminostyryl salts and the corresponding anils, hemicyanines, oxonols, open-chain dyes, and cyanine analogues derived from oxonium or sulphonium salts. The merocyanines are non-ionic acidic dyes, which were prepared from cyanine intermediate compounds and which are so important that they required Chapter XIV to themselves. Here they are grouped according to the length of chain, simple merocyanines, with the nuclei directly linked, being followed by sections on di-, tetra-, and hexa-methinmerocyanines. Next comes an account of quaternary salts of merocyanines, which are important in the preparation of trinuclear cyanines, then various types of merocyanines with a substituent on the chain are considered, and others in which part of the chain is cyclic. Variations in the nuclei which enter the merocyanine molecule include the use of unusual nuclei; modification of the chain led to aza analogues. A brief account of work on the colour of merocyanines is followed by one on open-chain related compounds. In Chapter XV, on trinuclear and polynuclear cyanines, most of the sections are preceded by a table summarising the various types included in the sub-sections. Chapter XVI is on the relationship between the colour and constitution of cyanines, and Chapter XVII deals with photographic sensitisation and other properties of these dyes.

In the index, the names of the heterocyclic nuclei are followed by their numbers in the second edition of *The Ring Index* (RRI). Where the ring is substituted, to give, for example, a di- or tetra-hydro derivative, the number reference is in a different form (see RRI).

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FRANCES M. HAMER

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